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Sensors and Actuators B 73 (2001) 130–134

SENSORS AND ACTUATORS B CHEMICAL

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A solid electrolyte hydrogen sensor with an electrochemically-supplied hydrogen standard

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Received 11 September 2000; received in revised form 4 October 2000; accepted 16 October 2000

Abstract

A high-temperature solid electrolyte hydrogen sensor consisting of two electrochemical cells was investigated. One cell was employed for electrochemical pumping of hydrogen from hydrogen-containing atmosphere and the other was used for sensing of the ambient hydrogen with the pumped hydrogen as a standard gas. On applying a voltage above 2.5 V to the pumping cell, a sufficient EMF response against hydrogen partial pressure was observed over a wide range of P_{H_2}. The required voltage of the pumping cell was affected by the hydrogen partial pressure in the test gas.

Keywords: Hydrogen sensor; Proton-conducting ceramics; Hydrogen pump; Hydrogen concentration cell

1. Introduction

$SrCeO_3$- and $CaZrO_3$-based oxides exhibit appreciable proton conduction under hydrogen-containing atmosphere at high temperatures [1–3]. Using these oxides as a solid electrolyte, high-temperature-type hydrogen sensor can be constructed [4,5]. A hydrogen sensor for molten metals has been developed and widely used in the process control in the metal melting industry [6,7]. However, the hydrogen sensor needs a standard gas with a known hydrogen pressure, e.g. 1% hydrogen argon-balanced gas, and thus the sensor system needs to equip the gas cylinder [6]. If such external standard material is excluded, it is possible to miniaturize the sensor device. Although molecular sieve, $AlPO_4 \cdot xH_2O$, etc. were examined as internal solid standard materials [5], long-time stability and reproducibility were still insufficient for a practical use. Hydrogen sensors based on the change in electrical conductivity of high-temperature-type protonic conductor have been studied [8–10].

Different from conductivity-type sensor, we have proposed a new-type steam sensor using two electrochemical cells [11]. One cell was employed for electrochemical pumping of hydrogen by means of electrolysis of water vapor in the atmosphere. Water vapor pressure could be determined from EMF of the other cell using the pumped hydrogen as a standard gas. In this paper, this working principle was applied to hydrogen sensor and the sensing performance was investigated.

2. Working principle of the hydrogen sensor

The working principle of the present hydrogen sensor is fundamentally the same as that in our previous paper of a steam sensor [11]. This principle of the hydrogen sensor is schematically illustrated in Fig. 1. The sensor consists of two proton-conducting electrolytes and a semi-closed gas compartment between the electrolytes. A constant voltage is applied to one cell to pump up hydrogen from a hydrogen-containing gas to be measured by the following electrode reactions.

Outer electrode of pumping cell < anode >

$$H_2 \rightarrow 2H^+ + 2e^-$$

Inner electrode of pumping cell < cathode >

$$2H^+ + 2e^- \rightarrow H_2$$

The hydrogen gas thus pumped was accumulated in a compartment between the pumping cell and the sensing cell. A small leakage is provided for the standard gas compartment, so that the hydrogen pressure in the compartment can be kept equal to the atmospheric pressure

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0925-4005/01/$ – see front matter
PII: S0925-4005(00)00672-9

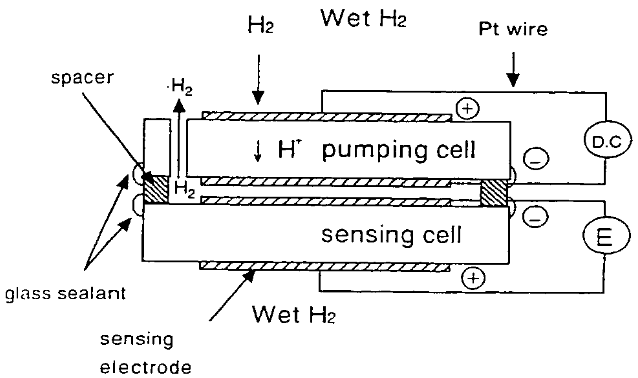

Fig. 1. A principle of a hydrogen sensor with an electrochemically-supplied hydrogen standard.

(1.0 atm). The other cell with a proton conductor generates EMF against the pumped hydrogen as a standard gas. The sensing cell can be expressed as

$$H_2(1.0\,\text{atm})_{\text{inside}},\ \text{Pt}|\text{electrolyte}|\text{Pt},\ \text{test gas}_{\text{outside}} \tag{3}$$

The EMF is based on the ratio of the hydrogen pressure in the standard gas compartment($P_{H_2} = 1.0$ atm) to that in the test gas $P_{H_2}(2)$:

$$E = \frac{RT}{2F} \ln \frac{P_{H_2}(1\,\text{atm})}{P_{H_2}(2)} \tag{4}$$

Therefore, P_{H_2} in the test gas can be determined from the measured EMF of the cell (3).

3. Experimental

The construction of the hydrogen sensor was essentially the same as that shown in Fig. 1. The proton-conducting oxides used for the pumping and the sensing cells were dense ceramics of $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$. Both surfaces of the ceramic discs (diameter: 14.5 mm, thickness of pumping cell: 0.5 mm, thickness of sensing cell: 1.0 mm) were adhered with porous platinum as an electrode material (electrode area of pumping cell: 0.6 cm^2, sensing cell: 0.5 cm^2). The ceramic of $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ for the pumping cell had a small open hole with a diameter of about 20 μm to leak excess amount of hydrogen from the standard gas compartment as shown in Fig. 1. Between the pumping and the sensing cells the spacer made of $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ was sandwiched with sealant. This spacer plays a role of electronic insulator to prevent the electronic contact between the pumping and the sensing electrodes. Direct current was sent to the pumping cell in a potentiostatic manner. EMF of the sensing cell was measured with an electrometer (HOKUTO DENKO HE-104). A mixture of hydrogen and argon was used as a sample gas and was saturated with water vapor at 20°C. The hydrogen partial pressure of the mixtured gas was determined by a gas chromatograph. The operating temperature was 700°C.

4. Results and discussion

4.1. The sensing performance

Fig. 2 shows the EMF of the sensing cell and the current density of the pumping cell plotted against the voltage applied to the pumping cell. P_{H_2} in the test gas was 0.081 atm. In this condition, protonic transport number in $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ is almost unity [1,12]. It is clear from this Fig. 2 that, when a voltage was applied to the pumping cell, the hydrogen was pumped from the test gas to the standard gas compartment, and the EMF of the sensing cell was increased. The EMF reached almost constant when a

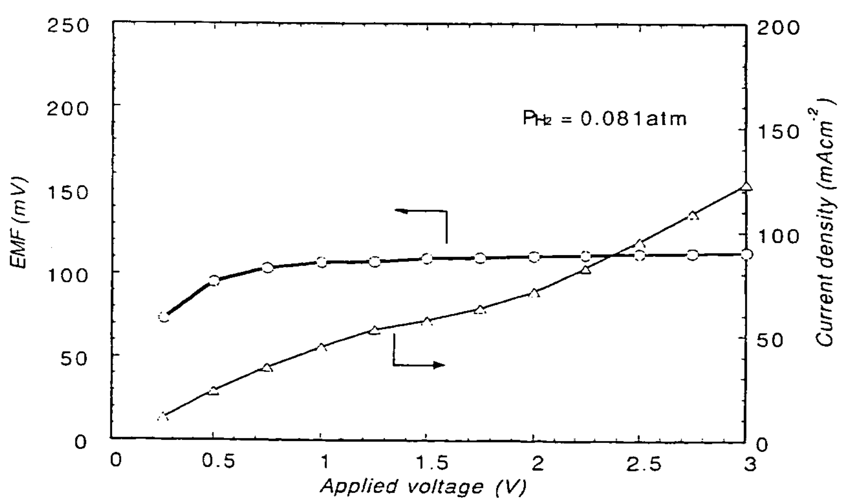

Fig. 2. EMF response of the sensing cell and the voltage–current relation of pumping cell at 700°C.

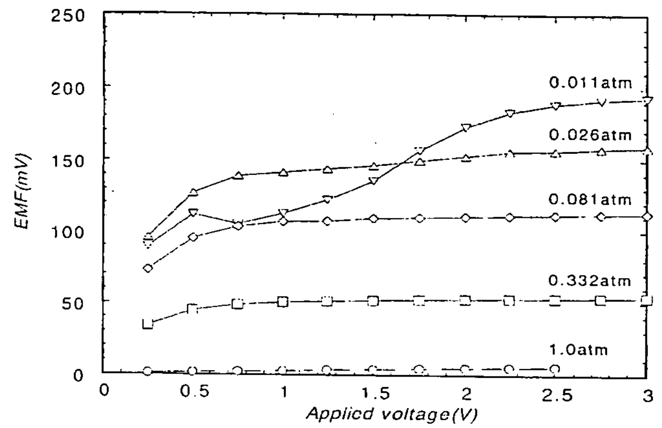

Fig. 3. EMF response of the sensing cell and applied to the pumping cell as a parameter of hydrogen parital pressure in the test gas (700°C).

voltage higher than 1.0 V was applied. This result suggests that the partial pressure of hydrogen in the standard gas compartment increased with the voltage and became constant when a sufficient voltage was applied to the pumping cell. Such dependence of EMF on the applied voltage was similar to that observed for the steam sensor previously reported by the authors [11].

Fig. 3 shows the relation between the EMFs of the sensing cell and the applied voltage of the pumping cell under various hydrogen partial pressures. All the EMFs increased with increasing applied voltage and became unchanged after certain voltages were applied. The values of applied voltage necessary to obtain constant EMF increased with partial pressure of hydrogen in the test gas.

EMF of the sensing cell with pumping voltages 2.0–3.0 V is plotted against logarithm of hydrogen partial pressure of the test gas in Fig. 4. Dashed line shows the theoretical EMF calculated from Eq. (4); the hydrogen pressure in the standard gas compartment is assumed to be 1 atm. The relation between the observed EMF and P_{H_2} was in good agreement with theoretical one when a voltage higher than 2.5 V was applied. This result indicates that the small open hole provided for the standard gas compartment is filled with hydrogen at 1 atm upon pumping a sufficient amount of hydrogen. The present hydrogen sensor, thus, worked in accordance with the presumed working principle described in Section 2, and could determine the partial pressures of hydrogen in the range from 1 to, at least, 0.01 atm.

4.2. *The response speed of the sensor*

EMF response was examined by changing hydrogen partial pressures in the test gas. Fig. 5 shows the time evolution of the EMF for test gases with P_{H_2} in the range of 0.011–1.0 atm; applied voltage for the pumping cell was 2.5 V. The EMF exhibited quick response against the changes in hydrogen partial pressures and indicated stable values. The time required to reach 90% of the final value was about 100 s. All the EMF values were close to the theoretical ones. When the circuit of the pumping cell was opened, the EMF of the sensing cell decreased slowly to 0 mV. This result indicates that the pumped hydrogen from the test gas flows away through the small hole and inversely the test gas with low content of hydrogen comes into the hole.

An initial response of the sensor was tested under a constant atmosphere of $P_{H_2} = 0.011$ atm in the test gas, and the result is shown in Fig. 6. Before applying the voltage to the pumping cell of the hydrogen sensor, a small uncertain EMF was observed which might be affected by a former measurement; as shown Fig. 5, it takes a long time to obtain the same atmosphere for the standard gas compartment and a test gas. However, on applying a voltage to the pumping cell, the EMF increased quickly and reached a theoretical value in 20 s.

In any cases, the response speed is very quick and it is sufficient for a practical use. This sensing performance depends on the size of the sensor cell, particularly, on the size of open hole of the pumping cell. Therefore, in the

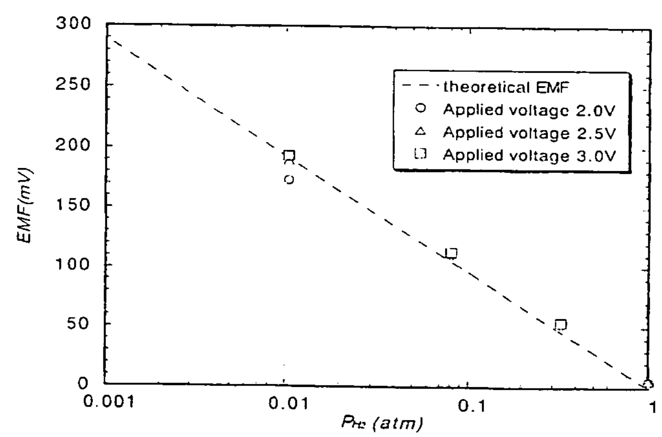

Fig. 4. EMF response of the sensor to hydrogen partial pressure in the test gas (700°C).

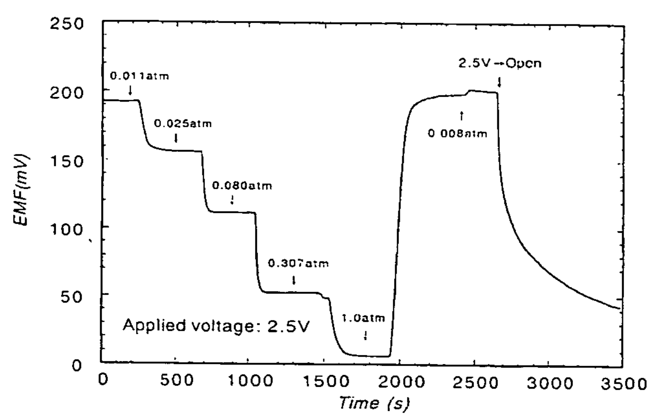

Fig. 5. EMF response of the hydrogen sensor at 700°C.

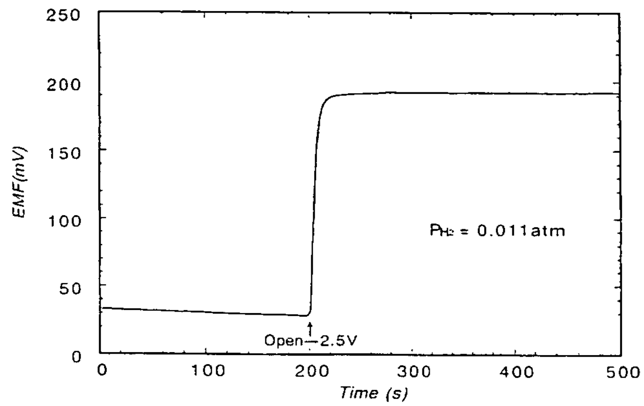

Fig. 6. EMF response of the hydrogen sensor at 700°C.

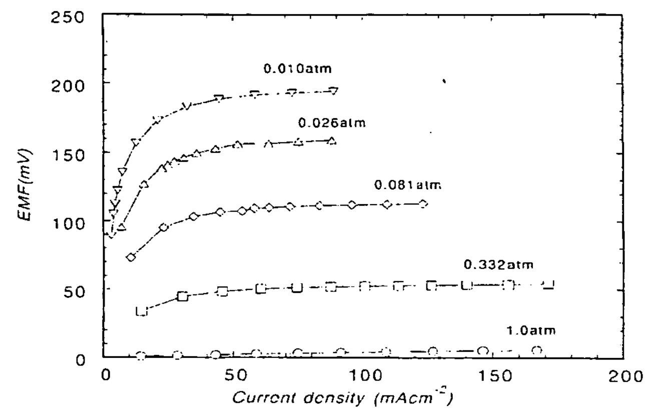

Fig. 8. Relation between EMF of sensing cell and current density of the pumping cell at 700°C.

future, it would be able to miniaturize sensor device and facilitate the handling.

4.3. Required voltages for the pumping cell

From the discussion in Section 4.2, it has become clear that this hydrogen sensor can be utilized for a practical use. However, applied voltages were relatively large. In order to clarify this reason, the relation between the current density and the applied voltage of the pumping cell was plotted in Fig. 7. Under low hydrogen partial pressure the current densities do not increase in the range of low applied voltage. This phenomenon suggests that hydrogen was hardly pumped in this applied voltage range. This reason is probably the concentration polarization of hydrogen [12]. Thus the large applied voltage was needed to detect hydrogen gas in low concentration.

To understand this phenomenon, the plot of the EMFs of the sensing cell against current density of the pumping cell was shown in Fig. 8. EMFs increased with increasing current density and they reached a constant value at almost the same current density despite the difference in hydrogen partial pressure. This result suggests that a certain current density is needed in maintaining the hydrogen partial pressure in the standard gas compartment. The applied voltage to obtain sufficient current density is different for a given hydrogen partial pressure in the test gas. Because of the concentration polarization of hydrogen at the anode of pumping cell and because of relatively large size of the hole, the large applied voltage needs to detect hydrogen in a low partial pressure in the test gas.

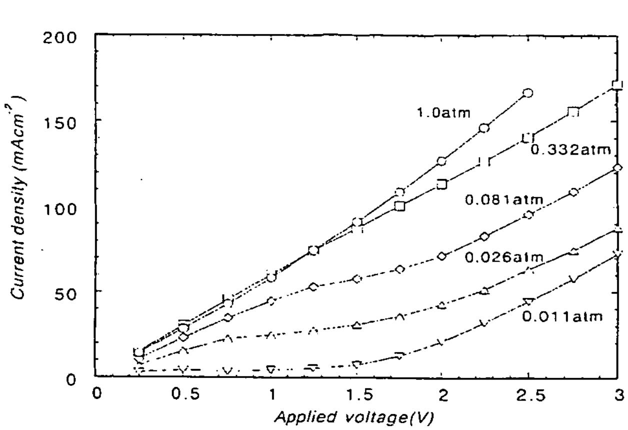

Fig. 7. Relation between current density and applied voltage of pumping cell at 700°C.

5. Conclusion

A high-temperature solid electrolyte hydrogen sensor using two electrochemical cells was investigated. On applying a voltage above 2.5 V to the pumping cell, the EMF of sensing cell reached the theoretical value for the hydrogen partial pressure of the test gas. The response speed of the sensor was very fast and would be sufficient for a practical use. A certain current density is needed for maintaining the hydrogen partial pressure of the standard gas compartment. The applied voltage to obtain sufficient current density is different for the hydrogen partial pressure in the test gas. Because of the concentration polarization of hydrogen and the size of the sensor cell, relatively large applied voltage is needed to detect low partial pressure of hydrogen in the test gas.

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